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Energetic Quaternary Salts Containing Bi(1,2,4-triazoles)

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New energetic salts (**2**, **3**, **9**, **10**, and **11**) were synthesized via the protonation of 4,4′-bi(1,2,4-triazole) or N-4-(1,2,4-triazole)-N-3-(4-methyl-1,2,4-triazole)amine with nitric acid or perchloric acid or 5-nitro-tetrazole. The structures of 4,4′-bi(1,2,4-triazolium) nitrate (**2**), N,N-dimethyl-N′-(5-methyl-tetrazole)methanimidamide (**8**), and N-4-(1,2,4-triazole)-N-3-(4-methyl-1,2,4-triazolium)amine perchlorate (**10**) were confirmed by a single-crystal X-ray analysis. The physical properties and heats of combustion of the new ionic salts were measured, and the heats of formation were also determined.

Introduction

Research on the synthesis of energetic materials has attracted much attention in recent years.[1−3] Most of the energy obtained from modern energetic materials results either from oxidation of the carbon backbone as traditionally found for energetic materials, such as HMX (1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane) and TNT (trinitrotoluene),[4] or from their high positive heats of formation, in such nitrogen-rich compounds as tetrazole azide[5] and 3,3′-azobis-(6-amino-1,2,4,5-tetrazine),[2] which exhibit standard heats of formation of +458 and +862 kJ/mol, respectively. Heterocycles that contain large amounts of nitrogen are typically relatively dense, and the smaller amounts of hydrogen and carbon enhance good oxygen balance. Normally, they also have higher heats of reaction. Recently, the syntheses of new heterocyclic-based energetic, low-melting salts were reported.[6,7] Energetic materials that are salt-based often possess advantages over nonionic molecules since they tend to exhibit very low vapor pressures, essentially eliminating the risk of exposure through inhalation, and ionic compounds often have higher densities than their atomically similar nonionic analogues.

Five-membered nitrogen-containing heterocycles are traditional sources of energetic materials, and considerable attention is currently focused on azoles as energetic compounds, especially the 1,2,4-triazole series.[8,9] N,N-linked biazoles have been synthesized and studied.[10,11] However, studies of the chemistry and properties of quaternary compounds of N,N-linked biazoles as energetic salts are limited. Now, we report the formation of the first quaternary salts of 4,4′-bi(1,2,4-triazole) or N-4-(1,2,4-triazole)-N-3-(4-methyl-1,2,4-triazole)amine by reaction with nitric or perchloric acid or 5-nitro-tetrazole and their structural, thermal, and thermodynamic properties.

Results and Discussion

4,4′-bi(1,2,4-triazole) (**1**) was synthesized according to the literature[10] from 4-amino-1,2,4-triazole and N,N-dimethyl-

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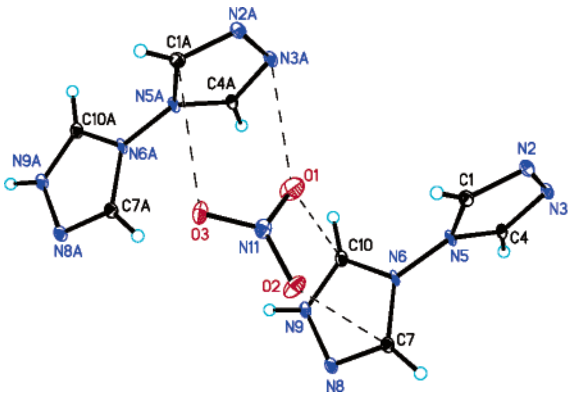
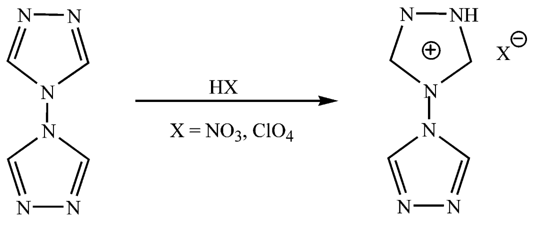


Figure 1. Plot showing the relative orientation of the NO_3 group to the cation. Dashed lines indicate close approaches. A second symmetry-generated $(1 + x, y, z)$ cation also shows its orientation relative to the NO_3 group. Thermal ellipsoids are shown at 30% probability. Hydrogen atoms are shown but are not labeled.

Scheme 1



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2, 3

formamide azine (**5**)[12] using *p*-toluenesulfonic acid as a catalyst. Initially, 1,1′-dimethyl-4,4′-1,2,4-triazolium diiodide was also prepared.[11] However, this quaternary dicationic salt was readily cleaved with water at 25 °C, precluding metathesis reactions in aqueous solutions of silver nitrate or perchlorate. Derivatives of 1,2,4-triazole can be quaternized with a strong acid (nitric or perchloric acid) to form corresponding salts.[6,7] In this case, 4,4′-bi(1,2,4-triazole) (**1**) was easily quaternized with 1 equiv of nitric or perchloric acid in a solution of methanol and acetonitrile (1:1 v/v) as the solvent to form the expected ionic salts **2** and **3**, in nearly quantitative yields and in high purity (Scheme 1). They melt at 150 and 187 °C, respectively. The structure of **2** was confirmed by a single-crystal X-ray analysis (Figure 1, Table 1). Compound **2** crystallizes in the monoclinic space group P2(1)/c with four molecules in the asymmetric unit. The compound consists of two crystallographically independent ions, 1H-4,4′-bi(1,2,4-triazolium) as well as the nitrate group. The two triazole rings are almost perpendicular to each other, with a dihedral angle of 92.4°. The linking N−N distances between the rings is 1.383(1) Å. One of the most notable features about this compound is the closeness and orientation of the nitrate anion to the organic cation. The nitrate group lies above the protonated triazolium ring and is canted at an angle of 58.4° to this ring. The O1−N11−O3 vector is somewhat aligned to the C7−C10 vector in the ring with short contacts between the cation and anion at O2···C7, 3.183 Å, and O1···C10, 2.790 Å. The O1−N11−O3 moiety of the nitrate group forms the same type of arrangement with the nearest symmetry-generated organic cation. In this case, the nitrate is canted at 82.0° to the plane of the triazole ring with slightly longer anion−cation distances: O1···N3, 3.004 Å, and O3···C1, 3.308 Å. This unusual arrangement of nitrate to cation has been observed recently in a similar compound, 1,5-diamino-4-methyltetrazolium dinitramide.[13] The multiple bonds appear to be localized in this protonated ring with C7−N8, 1.303(2) Å, and N9−C10, 1.301(2) Å. The shortest hydrogen bond is formed between the protonated nitrogen and the next-nearest nonprotonated ring: N9···N3^i, 2.693(1) Å ($i = x + 1$, $-y + {}^{3}/_{2}$, $z + {}^{1}/_{2}$ symmetry transformation). There are a variety of weak nonclassical hydrogen bonds to the nitrate group, ranging from 2.95 to 3.33 Å, which extend the system into a three-dimensional aggregate.

It was also found that even when 2.0 equiv of nitric acid was used [RT, methanol and acetonitrile (1:1 v/v) as solvent], the corresponding dinitrate salt was not obtained.

It is known that derivatives of tetrazole have possible applications as energetic components of propellants and gas-generating systems.[9,14] To introduce tetrazole derivatives into N,N-linked biazoles, 1-amino-5-methyltetrazole (**4**)[7a,15] and N,N-dimethylformamide azine (**5**) were reacted using reaction conditions identical to those for the formation of 4,4′-bi(1,2,4-triazole) (**1**), including *p*-toluenesulfonic acid as a catalyst and dry toluene as a solvent. However, the N,N′-linked target product 4-(5-methyl-tetrazole)-1,2,4-triazole (**6**) was not obtained. Rather, N-4-(1,2,4-triazole)-N-3-(4-methyl-1,2,4-triazole) amine (**7**) was formed in low yield (5%), and the main product was N,N-dimethyl-N′-(5-methyl-tetrazole)-methanimidamide (**8**) (Scheme 2). When H_2NOSO_3H was used as a catalyst, the yield of **7** was increased to 38% and **8** was also obtained concomitantly in high yield (50%) The structure of **8** was confirmed by a single-crystal X-ray analysis (Figure 2). It seems as if **5**, which is a kind of Schiff base, may have been hydrolyzed under acid-catalyzed conditions (*p*-toluenesulfonic acid or H_2NOSO_3H) to form N,N-dimethylformamide (DMF) and hydrazine in situ. Then, **8** was formed as the condensation product of 1-amino-5-methyltetrazole and DMF, with **7** being formed from **5** and hydrazine via a mechanism that is not clearly understood.

Compound **7** can be protonated with 1 equiv of nitric or perchloric acid or 5-nitro-tetrazole[16,17] in methanol as a solvent to form salts **9**, **10**, or **11** in high yield. A single-crystal X-ray structure determination of **10** clearly illustrates the influence of significant hydrogen bonding between the perchlorate anion and the protonated 1,2,4-triazolium ring (Figure 3). From the packing diagram, the structure is composed of inorganic perchlorate layers along the *bc* plane

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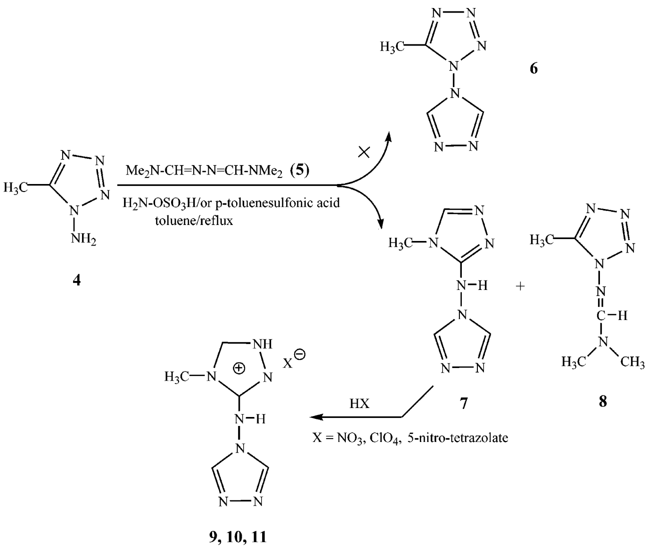
Table 1. Crystallographic Data for Compounds **2**, **8**, and **10**

formula	$C_4H_5N_7O_3$	$C_5H_{10}N_6$	$C_5H_{10}ClN_7O_5$
mol wt	199.15	154.19	283.65
cryst syst	monoclinic	orthorhombic	monoclinic
space group	P2(1)/c	Pbca	P2(1)/c
a (Å)	6.1135(11)	9.7829(5)	10.7575(8)
b (Å)	11.854(2)	12.1737(7)	6.0835(5)
c (Å)	10.575(2)	12.9452(7)	17.0340(14)
β (deg)	95.891(4)		96.701(2)
V (Å^3)	762.1(2)	1541.70(14)	1107.14(15)
Z	4	8	4
T (K)	86(2)	87(2)	86(2)
λ (Å)	0.710 73	0.710 73	0.710 73
ρ calcd (mg/m^3)	1.736	1.329	1.702
μ (mm^{-1})	0.149	0.094	0.376
F(000)	408	656	584
cryst size (mm^3)	0.47 × 0.47 × 0.08	0.35 × 0.30 × 0.08	0.22 × 0.10 × 0.03
θ range (deg)	2.59−25.24	3.10−25.25	1.91−25.00
index ranges	$-7 \leq h \leq 7, 0 \leq k \leq 14, 0 \leq l \leq 12$	$-11 \leq h \leq 11, -14 \leq k \leq 14, -15 \leq l \leq 15$	$-10 \leq h \leq 12, -7 \leq k \leq 7, -20 \leq l \leq 20$
No. reflns collected	13 250	17 276	8769
No. ind. reflns	1369	1398	1946
data/restraints/params	1369/0/128	1398/0/103	1946/0/168
GOF	1.096	1.086	1.083
R_1 [$I > 2\sigma(I)$]^a	0.0473	0.0406	0.0448
wR_2 [$I > 2\sigma(I)$]^b	0.1233	0.0989	0902
largest diff. peak, hole (e Å^{-3})	0.297, −0.333	0.319, −0.314	0.290, −0.320

[a] $R_1 = \Sigma|F_o| - |F_c|/\Sigma|F_o|$. [b] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

Scheme 2



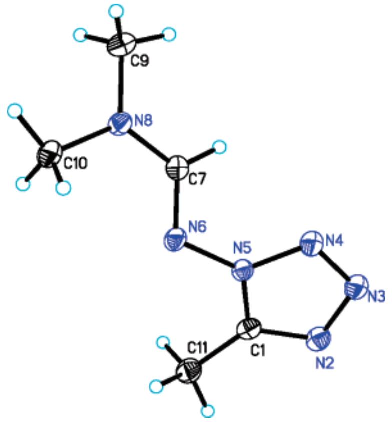


Figure 2. Molecular structure of compound **8** as a thermal ellipsoid (30%) plot.

that sandwich the organic bi-triazolium cations and water molecules. There is extensive hydrogen bonding within the organic/water layer, with the water molecules forming both donor and acceptor short hydrogen bonds to three different bi-triazolium cations (O5···N10, 2.82 Å; O5···N11, 2.88 Å; and N4···O5, 2.63 Å). Each bi-triazolium cation forms one weak hydrogen bond with the adjacent bi-triazolium cation (C9···N5, 3.23 Å), resulting in a twisted four-unit chain parallel to the *b* axis. These are linked, in turn, by the water molecules forming the extended organic layer. There are multiple hydrogen bonds to each perchlorate anion ranging from 2.83 to 3.31 Å. These tie the whole assembly together in an extended 3D array. The multiplicity of strong hydrogen bonding supports the high density of 1.85 g/cm^3 and melting point of 239 °C.

Derivatives of substituted triazoles were readily protonated with 5-nitro-tetrazole, which is a strong NH acid (pK_a for 5-nitro-tetrazole is −0.8),[18] to form corresponding ionic salts in high yields.[17] In this case, compound **11** was obtained from **7** and 5-nitro-tetrazole (Scheme 2). The melting point is 143 °C.

Densities and the standard enthalpies of formation are important properties of energetic salts. It can be seen from Table 2 that the densities for compounds with perchlorate as the anion are higher than that of the analogous nitrate; for example, the densities of the nitrate salt **9** and perchlorate salt **10** are 1.64 and 1.85 g/cm^3, respectively. Typical experimental results of constant volume combustion energies ($\Delta_c U_m$), calculated standard molar enthalpies of combustion ($\Delta_c H_m°$), and standard molar enthalpies of formation ($\Delta_f H_m°$) were obtained using a literature method[7] that was previously employed for similar salts. These values are included in Table 2. Comparing the standard molar enthalpies of formation ($\Delta_f H_m°$) of **2**, **3**, **9**, and **10**, it is seen that, when perchlorate is the anion, the standard molar enthalpy of formation of **3** or **10** is higher than those of the corresponding compounds

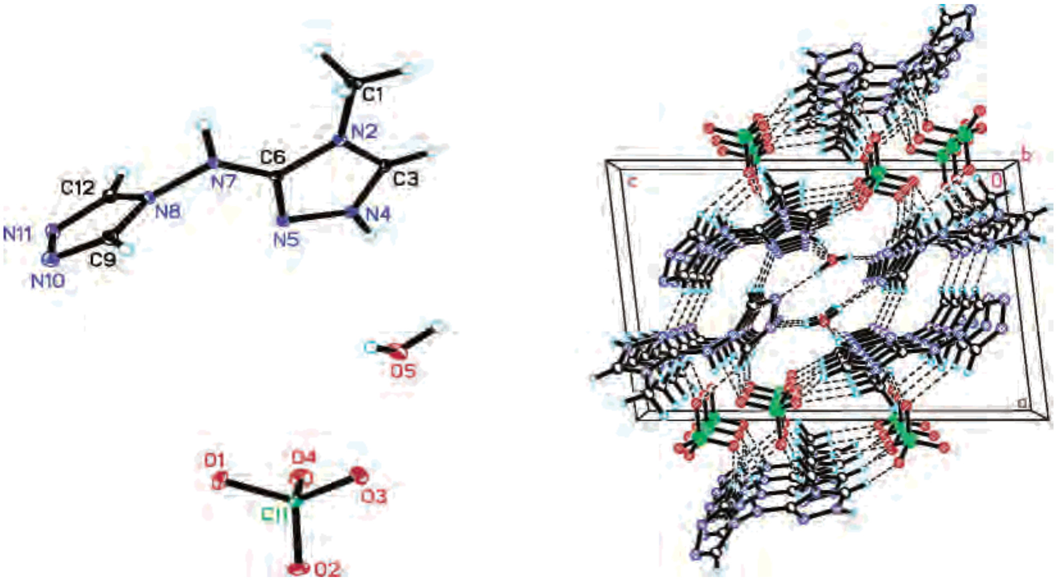


Figure 3. (a) Thermal ellipsoid plot (30%) of **10**. Hydrogen atoms are not labeled. (b) Packing diagram of **10** showing extensive hydrogen bonding (dashed lines).

Table 2. Phase Transition and Decomposition Temperatures, Densities, and Thermochemical Properties (at 298.15 K)

compd	T_m (°C)[a]	T_d (°C)[b]	d[c] (g/cm^3)	$-\Delta_c U_m$[d] (kcal/mol)	$-\Delta_c H_m°$[e] (kJ/mol)	$\Delta_f H_m°$[f] (kJ/mol)	$\Delta_f H_m°$[f] (kJ/kg)
2	150	150	1.73	576.7	2403.4	114.8	576.8
3	187	235	1.83	608.7	2534.4	296.4	1253.1
9	102	102	1.64	732.9	3057.6	−53.3	−232.5
10	239	265	1.85	732.9	3054.6	−5.7	−21.5
11	143	163	1.45	962.0	4012.4	508.0	1814.4

[a] Melting point (T_m). [b] Thermal degradation. [c] Measured density using gas pycnometer at 25 °C. [d] Constant volume combustion energy. [e] Molar enthalpy of combustion. [f] Molar enthalpy of formation.

with nitrate as the anion (**2** or **9**). The standard molar enthalpies of formation for **2** and **3** are higher than those for **9** and **10**. When 5-nitro-tetrazolate was the anion, the resulting compound, **11**, had the highest standard molar enthalpy of formation, 508.0 kJ/mol (1814.4 kJ/kg) of the compounds described.

Conclusions

New energetic bi(1,2,4-triazolium) salts were synthesized and characterized. N-4-(1,2,4-triazole)-N-3-(4-methyl-1,2,4-triazole)amine and its salts were obtained. Their calculated standard molar enthalpies of formation were lower than those of the N,N-linked bi(1,2,4-triazolium) salts. The melting points, thermal degradation temperatures, and the standard heats of formation for compounds with perchlorate as the anion are higher than those of the analogous nitrates, while the highest heats of formation were obtained when 5-nitro-tetrazolate was used as the energetic anion.

Experimental Section

General Methods. ^{1}H and ^{13}C NMR spectra were recorded on a 300 MHz nuclear magnetic resonance spectrometer operating at 300.13 and 75.48 MHz, respectively, with DMSO-d_6 as the solvent unless otherwise indicated. Chemical shifts were reported relative to Me_4Si. GC/MS spectra were determined using an appropriate instrument. Mass spectra for ionic salts were determined by using solid probe insertion. M^+ is the mass of the cation. The melting and decomposition points were recorded on a differential scanning calorimeter and a thermogravimetric analyzer at a scan rate of 10 °C/min, respectively. IR spectra were recorded using NaCl plates for neat liquids and KBr pellets for solids. Densities of ionic liquids were measured at 25 °C with a pycnometer. Densities of solid salts were measured at 25 °C using a Micromeritics Accupyc 1330 gas pycnometer. Elemental analyses were performed by the Shanghai Institute of Organic Chemistry.

Calorimetry Apparatus and Procedure. The heat of combustion was determined using a Parr (series 1425) semimicro oxygen bomb calorimeter. The substances were burned in an oxygen atmosphere at a pressure of 3.04 Mpa. The energy equivalent of the calorimeter was determined with a standard reference sample of benzoic acid (SRM 39i, N.I.S.T.). Since a Parr 45C10 alloy fuse wire was used, a correction of 2.3 (IT) calories per cm of wire burned has been applied in all standardization and calorific value determinations. Acid correction has been omitted for all semimicro samples. The bomb was examined for evidence of unburned carbon after each run, and if more than a slight trace was present, the run was discarded. The enthalpy of combustion was determined using the formula $\Delta_c H_m° = \Delta_c U_m + \Delta nRT$, where $\Delta_c U_m$ is the constant volume combustion energy and Δn is the increase in the number of moles of gas during the reaction. The molar enthalpies of formation, $\Delta_f H_m°$ at 298.15 K, of the corresponding ionic salts were calculated by designed Hess thermochemical cycles.

X-ray Crystallographic Studies. A crystal of compound **2**, **8**, or **10** was removed from the flask and covered with a layer of

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hydrocarbon oil. A suitable crystal was selected, attached to a glass fiber, and placed in a low-temperature nitrogen stream.[19] Data for **2**, **8**, and **10** were collected at 86, 87, and 86(2) K, respectively, using a Bruker/Siemens SMART APEX instrument (Mo Kα radiation, $\lambda = 0.710\ 73$ Å) equipped with a Cryocool NeverIce low-temperature device. Data were measured using omega scans of 0.3° per frame for 10, 20, and 20 s, and a full sphere of data was collected for **2** and **8**; a hemisphere of data was collected for **10**. A total of 2450, 2450, and 1471 frames were collected with a final resolution of 0.83 Å for all refinements. The first 50 frames were recollected at the end of data collection to monitor for decay. Cell parameters were retrieved using SMART[20] software and refined using SAINTPlus[21] on all observed reflections. Data reduction and correction for Lp and decay were performed using the SAINTPlus software. Absorption corrections were applied using SADABS.[22] Structures were solved by direct methods and refined by a least-squares method on F^2 using the SHELXTL program package. All non-hydrogen atoms were refined anisotropically. No decomposition was observed during data collection. Details of the data collection and refinement are provided in the Supporting Information.

4,4′-Bi(1,2,4-triazole) (1),[10] 1-amino-5-methyltetrazole (4),[7a,15] N,N-dimethyl-formamide azine (5),[12] and 5-nitro-tetrazole[16] were synthesized on the basis of literature methods.

4,4′-Bi(1,2,4-triazolium) Nitrate (2). A dried, nitrogen-filled Pyrex glass Schlenk tube was charged with **1** (0.136 g, 1.0 mmol), a mixture of methanol and acetonitrile (1:1 v/v, 4 mL), and concentrated nitric acid (70 wt %, 0.09 g, 1.0 mmol). The mixture was stirred for 2 h at 25 °C. The solvent was removed under a high vacuum overnight to leave a white solid: 98% yield, mp 150 °C. IR (KBr): 3122, 2971, 2410, 1969, 1754, 1579, 1517, 1348, 1280, 1180, 1090, 1066, 943, 891, 710, 611 cm^{-1}. ^{1}H NMR: δ 9.17 (s, 4H). ^{13}C NMR: δ 143.54. MS (solid probe; EI) *m/z* (%): 137 (M$^+$, 6.4). Anal. Calcd for $C_4H_5N_7O_3 \cdot H_2O$: C, 22.12; H, 3.22; N, 45.16. Found: C, 22.46; H, 2.90; N, 46.42.

4,4′-Bi(1,2,4-triazolium) Perchlorate (3). Compound **3** was prepared as above from **1** (0.136 g, 1.0 mmol) and concentrated perchloric acid (70 wt %, 0.15 g, 1.0 mmol) to give a white solid: 98% yield, mp 187 °C. IR (KBr): 3224, 3103, 2971, 2490, 2420, 2021, 1737, 1627, 1548, 1400, 1286, 1145, 1082, 918, 854, 785, 623 cm^{-1}. ^{1}H NMR: δ 9.16 (s, 4H). ^{13}C NMR: δ 143.53. MS (solid probe; EI) *m/z* (%): 137 (M$^+$, 8.5). HRMS (EI) calcd for cation $C_4H_5N_6$ (M$^+$) *m/z*: 137.0576. Found: 137.0572.

N-4-(1,2,4-Triazole)-N-3-(4-methyl-1,2,4-triazole)amine (7). Compound **7** was prepared as for **1**[10] from **4**[7] (0.99 g, 10 mmol) and **5**[12] (2.13 g, 15 mmol) using hydroxylamine-O-sulfonic acid (0.1 g, 0.9 mmol) as a catalyst, and these were refluxed for 72 h in 30 mL of dry toluene. Compound **7** was precipitated during the reaction and was obtained as a white solid: 38% yield, mp 286 °C. IR (KBr): 3082, 2966, 2912, 2717, 1944, 1628, 1508, 1470, 1414, 1348, 1309, 1249, 1220, 1171, 1036, 964, 866, 817, 777, 617 cm^{-1}. ^{1}H NMR (D_2O): δ 3.52 (s, 3H), 8.04 (s, 1H), 8.61 (s, 2H). ^{13}C NMR (D_2O): δ 156.33, 144.92, 143.90, 30.76. Anal. Calcd for $C_5H_7N_7$: C, 36.36; H, 4.27; N, 59.39. Found: C, 36.43; H, 4.29; N, 59.08.

N,N-Dimethyl-N′-(5-methyl-tetrazole)methanimidamide (8). Compound **8** was obtained from the same reaction in which **7** was formed, and it was recrystallized from hexane to form a white solid: 50% yield, mp 48 °C. IR (KBr): 2926, 2140, 1733, 1683, 1632, 1539, 1489, 1429, 1375, 1337, 1267, 1130, 1106, 1082, 974, 891, 692, 650 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 2.42 (s, 3H), 2.99 (s, 3H), 3.07 (s, 3H), 8.36 (s, 1H). ^{13}C NMR ($CDCl_3$): δ 157.30, 147.91, 42.26, 35.91, 9.42. Anal. Calcd for $C_5H_{10}N_6$: C, 38.96; H, 6.49; N, 54.55. Found: C, 39.05; H, 6.68; N, 54.32.

N-4-(1,2,4-Triazole)-N-3-(4-methyl-1,2,4-triazolium)amine Nitrate (9). Compound **9** was prepared as for **2** from **7** (0.17 g, 1.0 mmol) and concentrated nitric acid (70 wt %, 0.09 g, 1.0 mmol) to give a white solid: 98% yield, mp 102 °C. IR (KBr): 3305, 3103, 2760, 1624, 1572, 1309, 1384, 1308, 1215, 1154, 1089, 1061, 919, 849, 717, 669, 613 cm^{-1}. ^{1}H NMR (D_2O): δ 3.59 (s, 3H), 8.46 (s, 1H), 9.14 (s, 2H). ^{13}C NMR (D_2O): δ 157.30, 144.49, 142.93, 31.62. MS (solid probe; EI) *m/z* (%): 166 (M$^+$, 3.2). HRMS (EI) calcd for cation $C_5H_8N_7$ (M$^+$) *m/z*: 166.0841. Found: 166.0833.

N-4-(1,2,4-Triazole)-N-3-(4-methyl-1,2,4-triazolium)amine Perchlorate (10). Compound **10** was prepared as for **3** from **7** (0.17 g, 1.0 mmol) and concentrated perchloric acid (70 wt %, 0.15 g, 1.0 mmol) to give a white solid: 98% yield, mp 239 °C. IR (KBr): 3409, 3102, 2808, 2714, 1618, 1562, 1447, 1093, 819, 704, 627 cm^{-1}. ^{1}H NMR (D_2O): δ 3.61 (s, 3H), 8.53 (s, 1H), 9.15 (s, 2H). ^{13}C NMR (D_2O): δ 157.34, 144.57, 142.99, 31.76. MS (solid probe; EI) *m/z* (%): 166 (M$^+$, 2.8).

N-4-(1,2,4-Triazole)-N-3-(4-methyl-1,2,4-triazolium)amine 5-Nitro-tetrazolate (11). Compound **11** was prepared as above from **7** (0.17 g, 1.0 mmol) and 5-nitro-tetrazole[16] (0.115 g, 1.0 mmol) to give a white solid: 98% yield, mp 143 °C. IR (KBr): 3118, 2778, 1622, 1541, 1411, 1316, 1125, 1067, 965, 835, 668, 618 cm^{-1}. ^{1}H NMR (D_2O): δ 3.42 (s, 3H), 8.15 (s, 1H), 8.89 (s, 2H). ^{13}C NMR (D_2O): δ 168.02, 155.83, 143.86, 142.37, 30.69. MS (solid probe; EI) *m/z* (%): 166 (M$^+$, 3.0). Electrospray MS (+ve) $C_5H_8N_7$ *m/z*: (M$^+$), 166. MS (−ve) CN_5O_2 *m/z*: (M$^-$), 114.

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Supporting Information Available: X-ray crystallographic information files are available for 4,4′-bi-1,2,4-triazolium nitrate (**2**), N,N-dimethyl-N′-(5-methyl-tetrazole)-methanimidamide (**8**), and N-4-(1,2,4-triazole)-N-3-(4-methyl-1,2,4-triazolium)amine perchlorate (**10**). This information is available free of charge via the Internet at http://pubs.acs.org.

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